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(54) Lubricants for refrigeration compressors.

(57) Lubricant base compositions for compression refrigeration are composed of 95 to 5 percent by weight of polyether polyols having a number average molecular weight of from 400 to 5000 and from 5 to 95 percent of esters made from polyhydric alcohols with alkanoic acids or esters made from alkanedioic acids with alkanols. A refrigeration fluid is made from the base composition with the addition of selected hydrochlorofluorocarbons and hydrofluorocarbons so that the base composition is miscible with the refrigerant in the range of from -20 °C to greater than 65 °C.

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LUBRICANTS FOR REFRIGERATION COMPRESSORS

This invention relates to a blend of glycols and esters useful for lubricating heat pumps and air conditioning compressors.

Refrigerant R12 (dichlorodifluoromethane), is used in automotive air conditioners and many other types of refrigeration and air conditioning compressors. It is a chlorofluorocarbon that has been identified as depleting atmospheric ozone. The Montreal Accords restrict the production of R12 by 1990. Refrigerant R134a (1,1,1,2-tetrafluoroethane) has a vapor pressure that is very similar to R12 and it has the advantage that it does not deplete atmospheric ozone. R134a can replace R12 in most refrigeration systems without major redesign of present equipment. It could be used in automotive air conditioners without any re-tooling by the automotive companies.

The major problem of using R134a is that conventional lubricants such as naphthenic mineral oils are not soluble over the temperature range -20° to 80° C, the operating temperatures encountered in the different refrigeration applications. Some polyglycols are soluble in R134a at -25° C and below but phase separate below 60° C. Phase separation of the lubricant from the refrigerant can cause poor lubrication of the compressor which results in increased wear and decreased compressor life. It is well known in the refrigeration industry that lubricant concentration in the refrigerant is limited to the range of about 10 to 20 percent due to thermodynamic considerations. The usefulness of this invention is that it will enable compressor manufacturers to substitute R134a and other hydrofluorocarbons or hydrochlorofluorocarbons for chlorofluorocarbons such as R12 in most compressors without mechanical modification to existing compressors and be able to operate over a broad temperature range.

The fundamentals of lubrication in air conditioners are set forth by H.H. Kruse et al. in "Fundamentals of Lubrication in Refrigeration Systems and Heat Pumps" pages 763-783; ASHRAE Transactions Vol 90 part 2B (1984).

Lubricants for various air compressors are known from U.S. Patents 4,302,343 and 4,751,012. These patents show that various blends of esters and polyether polyols make a long lasting lubricant. However, these blends either have a neat viscosity less than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C or are immiscible at the high temperatures used in refrigeration.

U.S. Patent 4,755,316 discloses compositions containing one or more polyether polyols for lubricating refrigeration compressors using R134a. However, those compositions of the '316 patent which display adequate viscosity at the high temperatures in the compressor are not miscible at the same high temperature. Conversely, those compositions of the '316 patent which exhibit miscibility at the low temperatures are of too low a viscosity for adequate lubrication.

The invention comprises lubricant compositions that are miscible in hydrofluorocarbon and hydrochlorofluorocarbon refrigerants in the range of from -20° C to greater than 65° C and at the same time have a neat viscosity greater than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C.(100° F). In general, the compositions consist of

(A) from 5 to 95 percent of a polyether polyol which has the formula

$$Z\text{-}[(CH_2\text{-}CH(R_1)\text{-}O\text{-})_n\text{-}(CH_2\text{-}CH(CH_3)\text{-}O\text{-})_m\text{-}R_2]_p$$

where

Z is the residue of a compound having 1 to 8 active hydrogens,

R_1 is hydrogen, ethyl, or mixtures thereof,

n is 0 or a positive number,

m is a positive number,

n + m is a number having a value which will give a polyether polyol with a number average molecular weight range from about 400 to about 5000,

R_2 is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the the number of active hydrogens of Z, and

(B) from 95 to 5 percent of an ester selected from

(1) esters made from polyhydric alcohols with alkanoic acids, and

(2) esters made from alkanedioic acids with alkanols.

The neutral esters used in this invention are well known and/or available. Examples of suitable esters are the esters of dihydric alcohols, trihydric alcohols, and tetrahydric alcohols having 4 to 18 carbons such as glycerine, ethylene glycol, propylene glycol pentaerythritol, dipentaerythritol, tripentaerythritol, trimethylolpropane, trimethylolbutane, and trimethylolethane with alkanoic acids of from 4 to 18 carbon

atoms. These are illustrated by ethylene glycol distearate, propylene glycol dipelargonate, glycerine trioleate, trimethylolpropane triheptonate, and pentaerythritol tetraheptonate.

Also useful are the esters of monohydric alcohols having from 4 to 8 carbons with alkanedioic acids having from 4 to 18 carbons such as succinic, adipic, suberic, tetradecane 1,14-dioic acid, and hexadecane-1,16-dioic acid.

Examples of the polyether polyols or polyoxyalkylene polyols used in this invention are those derived from ethylene oxide, propylene oxide, 1-2, or 2-3 butylene oxide. The above oxides may be polymerized alone, i.e., homopolymerized or in combination. The combined oxides may also be combined in a random or block addition. While some of the above compounds may be of a hydrophilic nature, those of a hydrophobic nature are preferred, such as those derived from propylene oxide, butylene oxides or combinations thereof.

Examples of suitable capped polyoxyalkylene glycols are those derived from ethylene, propylene, and butylene oxides wherein the alkylene oxides are initiated from a compound having from 1 to 8 active hydrogens in a known manner. The terminal hydroxyl groups may be further reacted with alkyl halides to form alkyl capped polyoxyalkylene glycols. These polyether polyols and their preparation are well known from the book "Polyurethanes" by Saunders and Frisch, Interscience Publishers (1962), pages 33-39.

Examples of suitable initiator compounds which are employed to prepare the above polyether polyols are compounds having from 1 to 8 active hydrogens such as, for example, water, methanol, ethanol, propanol, butanol, ethylene glycol, propylene glycol, butylene glycol, 1,6-hexane diol, glycerine, trimethylol-propane, pentaerythritol, polyamines, sorbitol, sucrose and mixtures thereof.

Other initator compounds which are useful include monohydric phenols and dihydric phenols and their alkylated derivatives such as phenol, o, m, and p cresol, guaiacol, saligenin, carvacrol, thymol, o and p -hydroxy diphenyl, catechol, resorcinol, hydroquinone, pyrogallol and phloroglucinol.

Other initator compounds which are useful include ammonia, ethylene diamine, aminoethylethanolamine, N-aminoethylpiperazine, diethylenetriamine and triethylene tetramine.

The foregoing polyether polyols should have a number average molecular weight range of from 400 to 5000 and preferably in the range of from 500 to 1500.

The foregoing polyether polyols are blended to give a base lubricant composition containing from 5 to 95 weight percent of the esters and from 95 to 5 weight percent of the polyols with the ranges of from 70 to 90 polyols and from 30 to 10 esters being the preferred ranges, respectively.

The preferred polyether polyols are based on an initiator selected from glycerine or ethylene diamine and the preferred ester is a pentaerythritol tetraester of a mixture of alkanoic acids having from 7 to 9 carbons.

The final lubricant compositions of this invention may contain effective amounts of ashless additives, such as antioxidants, corrosion inhibitors, metal deactivators, lubricity additives, viscosity index improvers and extreme pressure additives as may be required.

Examples of useful ashless antioxidants which could be used herein are phenyl naphthylamines, i. ., both alpha and beta-naphthyl amines; diphenyl amine; iminodibenzyl; p,p-dibutyl-diphenylamine; p,p -dioctyldiphenylamine; and mixtures thereof. Other suitable antioxidants are hindered phenolics such as, for example, 6-t-butylphenol, 2,6-di-t-butylphenol and 4-methyl-2,6-di-t-butylphenol.

Examples of suitable ashless metal corrosion inhibitors are commercially available, such as N-oleoylsarcosine and Irgalube 349 from Ciba-Geigy which is an aliphatic amine salt of phosphoric acid monohexyl ester. Other useful metal corrosion inhibitors are NA-SUL DTA and NA-SUL EDS from the White Chemical Company (diethylenetriamine dinonylnapthalene sulfonate and ethylene diamine dinonylnaphthalene sulfonate), respectively.

Examples of suitable ashless cuprous metal deactivators are imidazole, benzimidazole, pyrazole, benzotriazole, tolutriazole, 2-methyl benzimidazole, 3,5-dimethyl pyrazole, and methylene bis-benzotriazole.

An effective amount of the foregoing additives for use in a refrigerant compression is generally in the range of from 0.1 to 5.0 percent by weight for the antioxidants, from 0.1 to 5.0 percent by weight for the corrosion inhibitors, and from 0.001 to 0.5 percent by weight for the metal deactivators. The foregoing weight percentages are based on the total weight of the polyether polyols and the esters. It is to be understood that more or less of the additives may be used depending upon the circumstance for which the final composition is to be used.

Examples of refrigerants useful in this invention are hydrochlorofluorocarbons such as chlorodifluoromethane, chlorofluoromethane, 2,2-dichloro-1,1,1-trifluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane, 2-chloro-1,1,2,2-tetrafluoroethane, 1-chloro-2,2,2-trifluoroethane, 1,1-dichloro-1-fluoroethane and 2-chloro-2,2-difluoroethane.

Examples of hydrofluorocarbon refrigerants useful in this invention are 1,1,1,2-tetrafluoroethane, 1,1,2,2-

tetrafluoroethane, 1,1,1-trifluoroethane, 2,2-difluoroethane, trifluoromethane, methylene fluoride, methyl fluoride, difluoroethylene and pentafluoroethane.

Several examples of the present invention with the refrigerant R134a (1,1,1,2-tetrafluoroethane) are given in Table II. Several control runs with the refrigerant R134a (1,1,1,2-tetrafluoroethane) are given in Table I. Table III illustrates the invention with other refrigerants such as R141b, R22, and R123.

The general procedure for the preparation of the controls and the examples was as follows. The selected polyol and ester were mixed and vacuum stripped. Glass ampoules were washed with acetone and vacuum dried at 110° C. The empty ampoule or tube was weighed and the mixture to be evaluated was syringed into the tube. The tube was re-weighed to determine the weight of lubricant. The tube was evacuated to remove air and then immersed in a dry ice/methylene chloride slurry in a Dewar flask. The R134a was transferred at a pressure of 8 psig (56 MPa gauge) into the tube to give the desired lubricant concentration. The filled ampoule was then disconnected and allowed to equilibrate at room temperature, 25° C. The ampoules were placed in a controlled temperature bath and the temperature varied from -20 to 85° C while observing for phase separation. The temperature of phase separation is called the upper solution critical temperature (USCT) and is reported in degrees C. Temperatures above 85° C were not investigated because of pressure limitations of the glass ampoule apparatus. Systems with USCT's above this temperature measurement limit are denoted as greater than 85° C.

Table I.

R134a Upper Solution Critical Temperature Data			
Run Number	Lubricant/Neat Viscosity, cs @ 100° F or 38° C (m^2/s)	Lubricant Wt % in R134a	USCT °C
Control A	100 Mobil P51 (Pentaerythritol tetraester of a mixture of alkanoic acids having 7-9 carbons) 25 (25×10^{-6})	25	80
Control B	100 Mobil P41 (Trimethylolpropane triheptonate) 15 (15×10^{-6})	16	>83
Control C	100 Emery 2914-D (Dimethyl azelate) 3 (3×10^{-6})	15	>85
Control D	100 L-1150 (n-butanol + PO to 1150 Mol Wt) 57 (57×10^{-6})	16	60
Control E	100 P-1000 (Propylene glycol + PO to 1000 Mol Wt) 73 (73×10^{-6})	25	70
Control F	100 P-2000 (Propylene glycol + PO to 2000 Mol Wt) 160 (16×10^{-5})	12	<25
Control G	70/30 P2000/P425 (n-butanol + PO to 425 Mol Wt) 95 (95×10^{-6})	15	45
Control H	70/30 L-1150/Emery 2914D 20 (2×10^{-5})	11	>70
Control I	70/30 P-2000/Mobil P51 87 (87×10^{-6})	13	<35
Control J	30/70 P-2000/Mobil P41 40 (4×10^{-5})	20	80

Table I shows that the esters and the polyols by themselves do not have both the required viscosity or USCT. Controls H, I and J show that even certain polyol/ester blends do not have the required viscosity to be effective.

Table II

R134a Upper Solution Critical Temperature Data			
Run Number	Lubricant/Neat Viscosity cs @ 100°F (m^2/s @ 38°C)	Lubricant Wt % in R134a	USCT °C
Example 1	90/10 CP700 (glycerine + PO to 700 mol wt) Mobil P51 89 (89×10^{-6})	9	>85
Example 2	90/10 CP700/Mobil P51 89 (89×10^{-6})	12	>85
Example 3	90/10 CP700/Mobil P51 89 (89×10^{-6})	17	80
Example 4	90/10 CP700/Mobil P51 89 (89×10^{-6})	22	80
Example 5	75/25 EDA511 (ethylene diamine + PO to 511 mol wt)/Mobil P41 203 (203×10^{-6})	8	>80
Example 6	75/25 EDA511 Mobil P41 203 (203×10^{-6})	19	>83
Example 7	75/25 EDA511 Mobil P41 203 (203×10^{-6})	29	>85
Example 8	75/25 EDA511 Mobil P51 245 (245×10^{-6})	9	>85
Example 9	75/25 EDA511 Mobil P51 245 (245×10^{-6})	11	>85
Example 10	75/25 EDA511 Mobil P51 245 (245×10^{-6})	20	>85
Example 11	70/30 CP1406(glycerine + PO to 1406 mol wt) Mobil P51 78 (78×10^{-6})	18	65

Table III.

Upper Solution Critical Temperature Data			
Run Number	Lubricant/Neat Viscosity cs @ 100° F (m^2/s @ 38° C)	Lubricant Wt % in Refrigerant	USCT °C
Example 12 with R141b	75/25 EDA511/Mobil P51 245 (245×10^{-6})	22	>65
Example 13 with R22	75/25 EDA511/Mobil P51 245 (245×10^{-6})	18	>65
Example 14 with R123	75/25 EDA511/Mobil P51 245 (245×10^{-6})	18	>65

Claims

1. A lubricant composition miscible in hydrofluorocarbon and hydrochlorofluorocarbon refrigerants in the range of from -20° to greater than 65° C and having a viscosity greater than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C comprising:

(A) from 95 to 5 percent of a polyether polyol which has the formula

$$Z\text{-}[(CH_2\text{-}CH(R_1)\text{-}O\text{-})_n\text{-}(CH_2\text{-}CH(CH_3)\text{-}O\text{-})_m\text{-}R_2]_p$$

where
Z is the residue of a compound having from 1 to 8 active hydrogens,
R_1 is hydrogen, ethyl, or mixtures thereof,
n is 0 or a positive number,
m is a positive number,
n + m is a number having a value which will give a polyether polyol with a number average molecular weight range of from 400 to 5000,
R_2 is hydrogen or an alkyl group of from 1 to 6 carbon atoms,
p is an integer having a value equal to the the number of active hydrogens of Z, and

(B) from 5 to 95 percent of an ester selected from
(1) esters made from polyhydric alcohols with alkanoic acids, and
(2) esters made from alkanedioic acids with alkanols.

2. A lubricant composition miscible in hydrofluorocarbon and hydrochlorofluorocarbon refrigerants in the range of from -20° to greater than 65° C and having a viscosity greater than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C comprising:

(A) from 95 to 5 percent of a polyether polyol which has the formula

$$Z\text{-}[(\text{-}CH_2\text{-}CH(CH_3)\text{-}O\text{-})_n\text{-}R]_p$$

where
Z is the residue of a compound having from 1 to 8 active hydrogens,
n is a number having an average value which will give a polyether polyol with a number average molecular weight range of from 400 to 5000,

R is hydrogen or an alkyl group of 1 to 6 carbon atoms,
p is an integer having a value equal to the number of active hydrogens of Z, and

(B) from 5 to 95 percent of an ester selected from
(1) esters made from polyhydric alcohols with alkanoic acids, and
(2) esters made from alkanedioic acids with alkanols.

3. A lubricant composition as claimed in Claim 2 wherein the polyether polyol is based on a residue selected from glycerine and ethylene diamine and the ester is a pentaerythritol tetraester of a mixture of alkanoic acids having from 7 to 9 carbons.

4. A fluid composition for use in compression refrigeration comprising

(A) a refrigerant selected from hydrochlorofluorocarbons and hydrofluorocarbons, and

(B) a lubricant composition as claimed in Claim 1 or Claim 2

5. A composition as claimed in Claim 4 wherein said fluid composition contains a concentration of from 1 to 30 percent by weight of lubricant composition.

6. A composition as claimed in Claim 4 wherein said hydrochlorofluorocarbons are selected from chlorodifluoromethane, chlorofluoromethane, 2,2-dichloro-1,1,1-trifluoroethane, 1-chloro-1,2,2,2-tetrafluoroethane, 2-chloro-1,1,2,2-tetrafluoroethane, 1-chloro-2,2,2-trifluoroethane, 1,1-dichloro-1-fluoroethane and 2-chloro-2,2-difluoroethane and said hydrofluorocarbons are selected from 1,1,1,2-tetrafluoroethane, 1,1,2,2-tetrafluoroethane, 1,1,1-trifluoroethane, 2,2-difluoroethane, trifluoromethane, methylene fluoride, methyl fluoride, difluoroethylene and pentafluoroethane.

7. A composition as claimed in Claim 4 wherein said hydrofluorocarbon is 1,1, 1,2-tetrafluoroethane.

8. A composition as claimed in Claim 4 wherein the polyether polyol is based on a residue selected from glycerine and ethylene diamine and the ester is a pentaerythritol tetraester of a mixture of alkanoic

acids having 7 to 9 carbons.

9. A process for preparing a lubricant composition miscible in hydrofluorocarbon and hydrochlorof luorocarbon refrigerants in the range of from -20° to greater than 65° C and having a viscosity greater than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C which comprises mixing :

(A) from 95 to 5 percent of a polyether polyol which has the formula

$$Z\text{-}[(CH_2\text{-}CH(R_1)\text{-}O\text{-})_n\text{-}(CH_2\text{-}CH(CH_3)\text{-}O\text{-})_m\text{-}R_2]_p$$

where

Z is the residue of a compound having from 1 to 8 active hydrogens,

R_1 is hydrogen, ethyl, or mixtures thereof,

n is 0 or a positive number,

m is a positive number,

n + m is a number having a value which will give a polyether polyol with a number average molecular weight range of from 400 to 5000,

R_2 is hydrogen or an alkyl group of from 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z, and

(B) from 5 to 95 percent of an ester selected from

(1) esters made from polyhydric alcohols with alkanoic acids, and

(2) esters made from alkanedioic acids with alkanols.

10. A process for preparing a lubricant composition miscible in hydrofluorocarbon and hydrochlorofluorocarbon refrigerants in the range of from -20° to greater than 65° C and having a viscosity greater than 75 centistokes (75 x 10^{-6} m^2/s) at 38° C which comprises mixing:

(A) from 95 to 5 percent of a polyether polyol which has the formula

$$Z\text{-}[(\text{-}CH_2\text{-}CH(CH_3)\text{-}O\text{-})_n\text{-}R]_p$$

where

Z is the residue of a compound having from 1 to 8 active hydrogens,

n is a number having an average value which will give a polyether polyol with a number average molecular weight range of from 400 to 5000,

R is hydrogen or an alkyl group of 1 to 6 carbon atoms,

p is an integer having a value equal to the number of active hydrogens of Z, and

(B) from 5 to 95 percent of an ester selected from

(1) esters made from polyhydric alcohols with alkanoic acids, and

(2) esters made from alkanedioic acids with alkanols.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 90 10 0379

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	US-A-4 302 343 (R. CARSWELL) * Claims 1,9; column 2, lines 45-65; column 3, lines 22-30 *	1-3,9, 10	C 10 M 111/04 C 10 M 169/04 C 09 K 5/04 // (C 10 M 111/04 C 10 M 105:36 C 10 M 105:38 C 10 M 105:62 C 10 M 107:34) (C 10 M 169/04 C 10 M 105:36 C 10 M 105:38 C 10 M 105:62 C 10 M 107:34 C 10 M 129:72 C 10 M 129:74 C 10 M 131:04 C 10 M 133:08) -/-
A		4,8	
X	EP-A-0 227 477 (THE DOW CHEMICAL CO.) * Claims 1-3,10; page 3, lines 5-20 *	1,2,9, 10	
D,A	US-A-4 755 316 (H. MAGID) * Claims 1,7; column 1, lines 5-10 *	1,2,4-7 ,9,10	
A	FR-A-2 388 227 (WESTING HOUSE ELECTRIC CORP.) * Page 5, lines 7-21; page 10, line 40 - page 11, line 21 *	1-5,8-10	
P,A	GB-A-2 216 541 (IMPERIAL CHEMICAL INDUSTRIES) * Claims 1,5,6; page 2, lines 8-25 *	1,2,4-7 ,9,10	
A	US-A-4 719 025 (K. AKIYAMA) * Claims 1,7 *	1,2,9, 10	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	US-A-4 248 726 (K. UCHINUMA) * Column 2, line 51 - column 3, line 65; column 5, lines 5-16; table 1 *	1-4,8-10	C 10 M C 09 K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	16-03-1990	HILGENGA K.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
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T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

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EUROPEAN SEARCH REPORT

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EP 90 10 0379

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
			C 10 N 40:30
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)

The present search report has been drawn up for all claims

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THE HAGUE	16-03-1990	HILGENGA K.J.

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